Ionic mixtures in two dimensions: from crystals to chain and dipole gases

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The ground state of a two-dimensional ionic mixture composed of oppositely charged spheres is determined as a function of the size asymmetry by using a penalty method. The cascade of stable structures includes square, triangular and rhombic crystals as well as a dipolar pair gas and a gas of one-dimensional crystalline chains. Thereby we confirm the square structure, found experimentally on charged granulates, and predict new phases detectable in experiments on granular and colloidal matter.

Predicting the crystalline structures from first principles is one of the key problems in condensed matter physics, material science, chemistry, geophysics and polymer physics [1]. For three-dimensional ionic crystals [2, 3], it is common textbook knowledge [4] that there are three basic equimolar structures whose stability depends on the ratio of the ion radii. For increasing asymmetry in the radii, the corresponding stability sequence involves the cesium-chloride, sodium-chloride, and zincblende structures. As indicated by the names, these structures are realized in nature for the (ionic) salt crystals $CsCl$, $NaCl$ and ZnS respectively, but they show also up for a number of other equal-valency salt crystals and for mesoscopic oppositely charged colloidal particles which are suspended in a strongly deionized solvent [5, 6, 7]. The stability is rationalized by minimizing the Madelung potential energy per particle pair with respect to various periodic equimolar candidate lattices at zero temperature and zero pressure.

In two spatial dimensions, a similar problem arises by exploring the ground-state structure of ionic crystal monolayers in a model of oppositely charged disks with different radii. In fact, three different realizations of two-dimensional ionic crystals are possible on microscopic, mesoscopic and macroscopic length scales. First of all, crystalline sheets of molecular salts can be deposited on smooth substrates by using e.g. electrochemical methods [8]. Secondly, oppositely charged colloidal particles [5, 6] can be confined to a single layer, e.g. by using laser-optical traps [9] or suspending them at a flat fluid-fluid interface [10]. Finally, there are granulate systems of millimeter-sized metallic balls which are oppositely charged and self-organize on a macroscopic plate into crystalline arrays [11, 12]. It is important to understand the different crystalline sub-structures both from a fundamental point of view and for applications. For example, a control of the composite structures of colloidal crystals leads to new photonic [13] or phononic [14] band-gap materials, to molecular-sieves [15], to micro- and nano-filters with desired porosity [16] and to nanowires composed of individual particle strings [17]. It allows to steer protein crystallization [18].

Despite its fundamental importance, the stability of two-dimensional ionic monolayers has not been addressed for asymmetrically sized ions. Previous theoretical studies have mainly focused on ionic criticality [19] at finite temperature and on equal ion size [20]. In this Letter, we predict the ground state structures for two different relevant set-ups of oppositely charged spheres: in the first, all centers of mass belong to a common plane which corresponds to a situation where both species are confined in an interface [16]. In the second set-up, all particle surfaces touch a common plane corresponding to spheres in contact with the same planar substrate where they are confined by e.g. gravity [11, 12]. Using a novel penalty method, a wealth of different stable structures is found. These include periodic crystalline arrays, on the one hand, with square, triangular and rhombic unit cells and with both touching and non-touching large spheres. On the other hand, a dipolar gas of particle pairs and a gas of particle chains with three different internal chain structures are also stable for strong size asymmetries in the substrate set-up. All these structures are detectable in experiments on granular and colloidal matter and in adsorbed crystalline layers of molecular salts.

The model system used in our study are equimolar $1:1$ mixtures of large ions (component A) with radius R_A carrying a positive charge q_A and small ions (component B) with radius R_B carrying a negative charge q_B ($|q_A| = |q_B| \equiv q$) such that the whole system is electroneutral. The size asymmetry $0 \leq R_B/R_A \leq 1$ is denoted with σ. These constitutive ions interact via a pairwise potential composed by a Coulombic and hard-core part

$$u_{\alpha\beta}(r) = \begin{cases} \frac{q_\alpha q_\beta}{r} & \text{if } r \geq R_\alpha + R_\beta \qquad (\alpha, \beta = A \text{ or } B) \\ \infty & \text{if } r < R_\alpha + R_\beta, \end{cases}$$

(1)

where r is the center-center distance between the ions α and β. The stability of the crystalline structure (at zero temperature) is ensured by steric interactions of the hardcore form. Our objective is to determine the stable structures at zero pressure and zero temperature by numerical minimization of the total potential energy.

Traditional minimization schemes [21, 22] typically re-

quire a continuous pairwise potential form in order to localize the minimum. The discontinuous hard-core potential splits the parameter space into various distinct regions which hampers straight-forward numerical minimization. For potentials which involve a hard-core part we have developed here a new technique to overcome this difficulty that relies on the so-called *penalty* method [23] which was hitherto applied to geometric packing problems of hard bodies. The key idea is to relax the non-overlap condition (i.e., $r \geq R_\alpha + R_\beta$) by introducing an auxiliary penetrable pair interaction:

$$v_{\alpha\beta}(r) = \frac{q_\alpha q_\beta}{r} + \mu \max(R_\alpha + R_\beta - r, 0), \qquad (2)$$

where $\mu > 0$ is a penalty parameter which is larger than the gradient of the potential at contact. This parameters gives a finite energy penalty to any overlapping configuration. If μ is finite but sufficiently large, the total potential energy for the auxiliary potential $v_{\alpha\beta}(r)$ has exactly the same minimal configuration as that for $u_{\alpha\beta}(r)$. However, numerically the potential energy landscape is now continuous such that standard minimization routines like the simplex algorithm [24] can be applied. Though the penalty technique itself is applicable to any spatial dimensionality and hard particle shape, we exploit it here to predict the ground state for binary hard charged spheres.

In detail, we consider a parallelogram as a primitive cell which contains n_A A-particles and n_B B-particles. We restrict ourselves to the case $n_A < 3, n_B < 3$. This cell can be described geometrically by the two spanning lattice vectors $\mathbf{a}$ and $\mathbf{b}$. The position of a particle i (of species A) and that of a particle j (of species B) in the parallelogram is specified by the vectors $\mathbf{r}_i^A = (x_i^A, y_i^A)$ and $\mathbf{r}_j^B = (x_j^B, y_j^B)$, respectively. Thereby, the new potential energy function that needs to be minimized at zero pressure and zero temperature as a function of the crystalline lattice parameters reads

$$U_{\text{total}} = \frac{1}{2} \sum_{\alpha=A,B} \sum_{i,j=1}^{n_\alpha} \sideset{}{'}\sum_{\mathbf{L}} v_{\alpha\alpha}(\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha + \mathbf{L})$$
$$+ \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \sum_{\mathbf{L}} v_{AB}(\mathbf{r}_i^A - \mathbf{r}_j^B + \mathbf{L}), \qquad (3)$$

with $\mathbf{L} = k\mathbf{a} + l\mathbf{b}$ where k and l are integers. The sums over $\mathbf{L}$ in Eqn. 3 run over all lattice cells where the prime indicates that for $\mathbf{L} = 0$ the terms with $i = j$ are to be omitted. In order to handle efficiently the long range nature of the Coulomb interaction, we employed a Lekner-summation [25].

We now consider two different set-ups, the "interfacial model" and the "substrate model". In the interfacial model which can be considered as a purely two-dimensional situation, the centres of all spheres are confined to a plane, see Fig. 1(a) for a side view of a configuration. In the substrate model, on the other hand, all

spheres are touching the same underlying plane, see Fig. 3(a) for a side view of a configuration.

For the interfacial model, the stability phase diagram is shown versus the size asymmetry σ in Fig. 1(b). By increasing σ, the following phase cascade occurs:

$$\triangle(\text{touching, } N_c = 2) \rightarrow \triangle(\text{touching, } N_c = 3) \rightarrow$$
$$\triangle(\text{non-touching, } N_c = 3) \rightarrow Rh(\text{touching, } N_c = 3) \rightarrow$$
$$\square(\text{touching, } N_c = 4) \rightarrow \square(\text{non-touching, } N_c = 4)$$

where the symbols $\triangle$ and $\square$ stand for triangular and square unit cells of the big ions A, respectively, and Rh corresponds to rhombic unit cells, as illustrated by the top views of the crystalline structures in Fig. 1(b). The topological aspect of these four phases can be discussed in terms of contact between the large spheres. More specifically, a "touching" configuration involves connected big spheres while a "non-touching" one implies disconnected big spheres, see Fig. 1(b). In particular, the "touching" triangular and rhombic phases are both characterized by connected A-spheres in contrast to the "non-touching" $\triangle$ and $\square$ structures which possess disconnected large spheres. Additionally, the ionic coordination number N_c defined by the number of A particles touching a single B particle, is another relevant topological characteristic.

As far as the phase transitions reported in Fig. 1 are concerned, the following scenario takes place. At vanishing small ion size ($\sigma \rightarrow 0$), the small ions get squeezed between two big ions so that the three centers of mass lie on a same line. The first transition $\triangle(\text{touching, } N_c = 2) \rightarrow \triangle(\text{non-touching, } N_c = 3)$ via the special structure $\triangle(\text{touching, } N_c = 3)$, characterized by an increase of the number of contacts between A and B ions, occurs at $\sigma = \frac{2}{\sqrt{3}} - 1$. This special point corresponds to a compact triangular structure where a small ion has three contacts with neighbouring big ions, allowing a continuous transition. The second transition, $\triangle(\text{non-touching, } N_c = 3) \rightarrow Rh(\text{touching, } N_c = 3)$, occurring at $\sigma = 0.297$ is discontinuous as signaled by a jump of the angle between the two adjacent sides of the unit cell. The third transition $Rh(\text{touching, } N_c = 3) \rightarrow \square(\text{non-touching, } N_c = 4)$ via $\square(\text{touching, } N_c = 4)$, occurring at $\sigma = \sqrt{2} - 1$ is continuous. A remarkable feature, en passant, is the stability of the square phase over a wide range of the size ratio σ.

For the two non-touching phases ($\triangle, \square$) one can assign two new Madelung constants M associated to the (lattice) electrostatic energy per molecule (i.e., a pair of ions A and B) $E = -M \frac{q^2}{R_A + R_B}$. Lekner sums carried on the appropriate lattices provide:

$$M_\triangle = 1.542, \quad M_\square = 1.616$$

for the non-touching triangular and square structures, respectively. As expected, this reported value of $M_\square$ lies perfectly between that of the one dimensional lat-
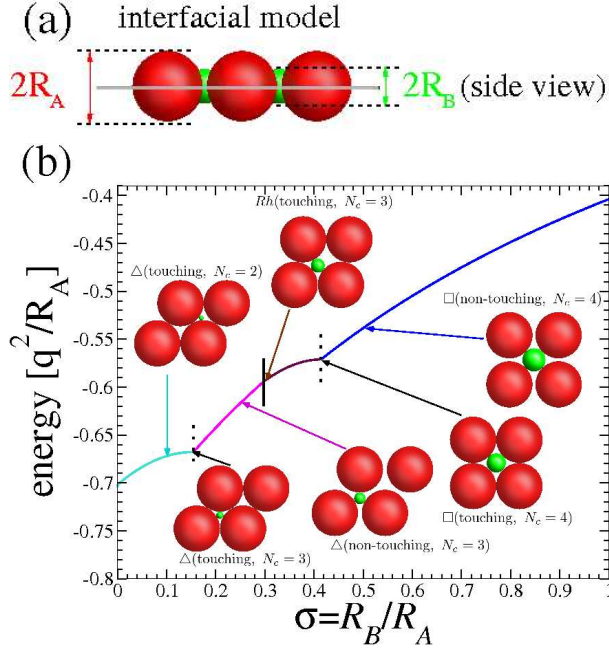
FIG. 1: Stable structures of oppositely charged spheres versus their size asymmetry $\sigma = R_B/R_A$ in the interface model, where all sphere centers fall on the same plane: a) side-view, b) (scaled) energy per ion. The discontinuous transition is indicated by a solid bar. Continuous transitions are denoted by a broken bar. Unit cells of the corresponding stable phases are shown, where the big (small) have a radius R_A (R_B).

tice ($M_{1D} = 2\ln 2$) and that of a three-dimensional one ($M_{NaCl} = 1.747$).

Next we focus on the area fraction covered by the spheres which is defined as $\phi = \frac{\pi(R_A^2 + R_B^2)}{S_{cell}}$, with S_{cell} being the (projected) surface of the unit cell. The results are sketched in Fig. 2. In the regime $\sigma < \frac{2}{\sqrt{3}} - 1$ corresponding to compact triangular structures, there is enough space to host a small ion in the interstice offered by the touching big ions, so that the profile is identical to that of pure hard disk systems, where $\phi = \frac{\pi(1+\sigma^2)}{2\sqrt{3}}$. In other words the location of the small sphere within the interstice does not alter the packing fraction. For non-touching triangular structures ($\frac{2}{\sqrt{3}} - 1 < \sigma < 0.297$), ϕ varies like $\frac{2\pi(1+\sigma^2)}{3\sqrt{3}(1+\sigma)^2}$. In the rhombic phase regime ($0.297 < \sigma < \sqrt{2} - 1$), the shape as well as the surface of the unit cell vary in a non-trivial manner. For large enough small ions, in the square phase regime, ($\sqrt{2} - 1 < \sigma < 1$), ϕ is given by $\frac{\pi(1+\sigma^2)}{2(1+\sigma)^2}$.

We finally present results for the "substrate model" where all spheres are touching the same underlying substrate plane, see Fig. 3(a) for a side-view. The stable crystalline structure and their energy per ion is shown in Fig. 3(b) versus the diameter ratio σ. For increasing size
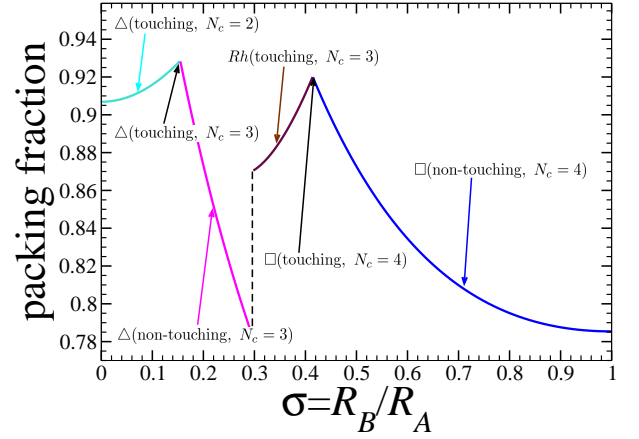

FIG. 2: Area fraction as a function of the size aspect ratio $\sigma = R_B/R_A$.

asymmetry σ, a cascade of six structures is found:

$$\text{dipolar gas (non-touching, } N_c = 1) \rightarrow$$
$$\text{chain gas (non-touching, } N_c = 1) \rightarrow$$
$$\text{chain gas (touching, } N_c = 1) \rightarrow$$
$$\text{chain gas (touching, } N_c = 2) \rightarrow$$
$$\text{chain gas (non-touching, } N_c = 2) \rightarrow$$
$$\triangle\text{(non-touching, } N_c = 3) \rightarrow \square\text{(non-touching, } N_c = 4)$$

In the limit of very large asymmetry ($\sigma \rightarrow 0$), dipoles perpendicular to the substrate plane are formed. Such parallel dipoles repel eachother and arrange into a crystal with diverging lattice constant and a coordination number $N_c = 1$. We call this state a "dipole gas". When σ increases, the dipole moments are getting gradually tilted relative to the substrate normal until a first-order transition towards a chain composed of dipolar pairs occurs where the individual dipoles are non-touching and the coordination numbers stays at $N_c = 1$. The distance between neighbouring chains diverges since they are mutually repulsive. We are dealing therefore with a "chain gas" at infinite dilution, i.e. the system is periodic in the direction along the string but with a diverging interchain distance perpendicular to it bearing some analogy to smectic dipolar sheets [26]. Upon increasing σ more, the chain structure changes continuously to an internal conformation with touching large spheres (still with $N_c = 1$). This structure then transforms continuously into a chain gas of non−touching large spheres with $N_c = 2$. Then, there are two crystalline structures appearing known already from the interface model, namely a non-touching $\triangle$ and a non-touching $\square$ lattice. The former has only a tiny stability domain while the latter is stable along an enormous range of $0.517 < \sigma \leq 1$. We emphasize the striking emergence of the gas phases in the substrate model which are absent in the interface model and in three dimensions.
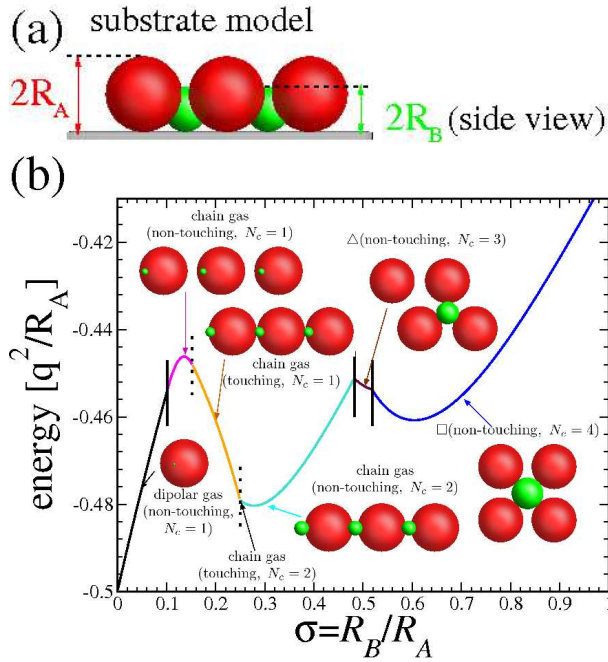
FIG. 3: Stable structures of oppositely charged spheres versus their size asymmetry $\sigma = R_B/R_A$ in the substrate model, where all sphere surfaces touch the same plane: a) side-view, b) (scaled) energy per ion. Discontinuous transitions between the structures are indicated by a solid bar. Continuous transitions are denoted by a broken bar. Bottom views of the unit cells of the corresponding stable phases are displayed, where the big (small) have a radius R_A (R_B).

In conclusion, we have explored the stable ground state structures of two-dimensional ionic crystals for an "interface" and a "substrate" set-up at zero pressure. For a 1:1 oppositely charged mixture of spheres with different diameters, various stable crystalline phases were identified including periodic crystals and chain and dipolar gases. Apart from adsorbed molecular salt systems, the structures of the interface set-up can be verified in suspensions of oppositely charged particles. The substrate set-up, on the other hand, is realized for oppositely charged granular matter on a plane. Recent experiments on oppositely charged granular sheets with $\sigma \approx 1$ [11, 12] have indeed revealed a stable $\square$(non-touching) configuration which is confirmed by our calculations. More experimental investigations on systems with higher size asymmetry are performable and could open the way to see the $\triangle$(non-touching) and the predicted chain and dipolar gases.

The penalty method can in principle be applied to any other potentials which involve hard-body parts, both in two and in three dimensions. It would be interesting to see the stability phase diagram for different mixtures as e.g. colloidal hard-spheres mixtures with or without added nonadsorbing polymers.

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